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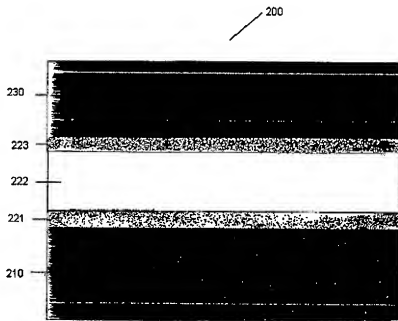
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(54) Title: METAL ORGANIC CHEMICAL VAPOR DEPOSITION AND ATOMIC LAYER DEPOSITION OF METAL OXYNITRIDE AND METAL SILICON OXYNITRIDE



(57) Abstract: The invention is directed to gate and capacitor dielectrics for use in making advanced high-g stack structures. According to the invention, a metal alkylamide is used in a MOCVD or ALD process to create metal oxynitride or metal silicon oxynitride dielectric film. The metal oxynitride or metal silicon oxynitride films can be positioned between a silicon substrate and a doped polycrystalline silicon (Poly Si) or a metal electrode layer.

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## **METAL ORGANIC CHEMICAL VAPOR DEPOSITION AND ATOMIC LAYER DEPOSITION OF METAL OXYNITRIDE AND METAL SILICON OXYNITRIDE**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is related to, and claims priority to, United States Provisional Patent Application No. 60/396,744, entitled Metal Organic Chemical Vapor Deposition and Atomic Layer Deposition of Hafnium [sic] or Zirconium Oxynitride and Hafnium [sic] or Zirconium Silicon Oxynitride, filed July 19, 2002, the entire disclosure of which is hereby incorporated by reference.

### **FIELD OF THE INVENTION**

The present invention relates generally to the field of semiconductor fabrication. More specifically, the present invention relates to metal organic chemical vapor deposition ("MOCVD") and atomic layer deposition ("ALD") of metal oxynitride (Hf-O-N) and metal silicon oxynitride layers to form gate and capacitor dielectrics.

### **BACKGROUND OF THE INVENTION**

The speed and functionality of computers continues to improve every year, facilitated in large part by shrinking dimensions of integrated circuits. Currently, the smallest dimension in modern circuits is the thickness of the gate insulator, which separates the controlling electrode ("gate electrode") from the controlled current in the silicon. Traditionally, the gate dielectric has been made from silicon dioxide (SiO<sub>2</sub>)

and/or silicon nitride (SiN). Such dielectrics are now as thin as 1.5 nm or 4 atomic layers. Further reduction would cause current to leak through the insulator by quantum-mechanical tunneling. Accordingly, efforts are underway to find alternative dielectric materials. To date, efforts have focused largely on high dielectric constant (high "k") materials. As used herein, a material is "high k" if its dielectric constant "k" is higher than the dielectric constant of silicon oxide (k approximately 3.9).

In addition, efforts have focused on better methods for depositing metallic materials in pure form with uniform stoichiometry, thickness, conformal coverage, abrupt interface, smooth surface, and reduced grain boundaries, cracks and pinholes. MOCVD and ALD are examples of two methods that have been developed.

In CVD, precursors and co-reactants are brought together at the surface of the growing film. Layer thickness is controlled by controlling the concentration of precursors and co-reactants in the reaction chamber, the temperature of the reaction chamber and the temperature of the substrate. In MOCVD, the precursor is a metal organic compound. Metal organic precursors are superior to metal inorganic precursors because they are less corrosive, require less extreme reaction conditions, and provide less contamination in the resulting film.

In ALD, precursors and co-reactants are brought to the surface of the growing film separately, through alternating pulses and purges, to generate one mono-layer of film growth per pulse cycle. Layer thickness is controlled by the total number of pulse cycles.

A number of publications have reported high k dielectric materials formed from metal oxynitrides or metal silicon oxynitrides where the metal is hafnium or zirconium (collectively "hafnium/zirconium (silicon) oxynitrides"). See U.S. Patent Nos. 6,291,867 B1, 6,291,866 B1, 6,020,243, 6,020,243, and 6,013,533 (collectively "the Wallace patents"); see also *Reliability Evaluation Of HfSiON Gate Dielectric Film With 12.8 Å SiO<sub>2</sub> Equivalent Thickness*, A. Shanware et al., 2001 IEEE; see also *Properties Of Hf-Based Oxide And Oxynitride Thin Films*, M. R. Visokay et al., 2002 AVS 3<sup>rd</sup> International Conference on Microelectronics and Interfaces, February 11-14, pp. 127-129; see also *Application Of HfSiON As A Gate Dielectric Material*; M.R. Visokay et al., *Applied Physics Letters*, vol. 80 No. 17, pp. 3183-3185 (April 29 2002); see also *Electrical Characteristics Of ZrO<sub>x</sub>N<sub>y</sub> Prepared By NH<sub>3</sub> Annealing Of ZrO<sub>2</sub>*, S. Jeon et al., *Applied Physics Letters*, vol. 79, No. 2, pp. 245-247 (July 2001); and see

also *Thermally Stable Ultra-Tin Nitrogen Incorporated  $ZrO_2$  Gate Dielectric Prepared By Low Temperature Oxidation Of  $ZrN$* , M. Koyama et al., 2001 IEEE. In each of these publications, reactive sputtering is the deposition technique. Reactive sputtering is not a viable technique for the commercial deposition of high k gate dielectrics due to the relatively high vacuum conditions required. Only the Wallace patents suggest using CVD as an alternative technique. However, Wallace directs the reader to metal chloride precursors, such as hafnium tetrachloride ( $HfCl_4$ ) or zirconium tetrachloride ( $ZrCl_4$ ), and nitrogen bearing precursors, such as hafnium nitrate ( $Hf(NO_3)_3$ ) or zirconium nitrate ( $Zr(NO_3)_2$ ). Accordingly, Wallace does not teach a MOCVD or ALD process for making high k zirconium/zirconium (silicon) oxynitride dielectrics. Furthermore, Wallace does not use of ozone as an oxygen source.

The use of metal alkyl amide precursors in MOCVD and ALD has been reported. For example, zirconium alkyl amides have been used in a MOCVD process to deposit silicates and oxides hafnium and zirconium. See *Alternating Layer Chemical Vapor Deposition (ALD) Of Metal Silicates And Oxides For Gate Insulators*, R. Gordon et al., Mat. Res. Soc. Symp. Proc. Vol. 670, 2001 Materials Research Society, pp. K2.4.1-K2.4.6; see also *Effects Of Deposition Conditions On Step-Coverage Quality In Low-Pressure Chemical Vapor Deposition of  $HfO_2$* , Y. Ohshita et al., J. of Crystal Growth, 235 (2002) pp. 365-370; see also *Atomic Layer Deposition of Hafnium Dioxide Films from Hafnium Tetrakis(ethylmethanamide) And Water*, K. Kukli et al., Chem. Vap. Deposition, 2002, 8, No. 5, pp. 199-204. Also, the instant inventor has used tantalum alkyl amides in an MOCVD process to form tantalum nitride. See *MOCVD Of High-K Dielectrics, Tantalum Nitride And Copper*, Y. Senazaki et al., Adv. Mater. Opt. Electrn., vol. 10, pp. 93-103 (2000). However, the use of metal alkyl amides as metal organic precursors in a MOCVD or ALD process for forming hafnium/zirconium (silicon) oxynitrides has not been reported.

As the use of high k dielectric materials have found application in the industry, limitations have surfaced. For example, while hafnium based dielectric materials are considered a promising candidate due to its high dielectric constant (k approximately 20) and good thermal stability, undesired interfacial silicon oxide ( $SiO_x$ ) layers tend to form at the interface with the silicon substrate during post deposition thermal treatments such as annealing. Further, high k stack dielectrics are finding use in the industry. For example, the preparation of high quality tantalum oxynitride ( $TaO_xN_y$ )

with zirconium silicate ( $\text{ZrSi}_x\text{O}_y$ ) as an interfacial layer for use in gate dielectric applications has been reported. See *Electrical Characteristics of TaOxNy/ZrSiOy Stack Gate Dielectric for MOS Device Applications*, H. Jung et al., Mat. Res. Soc. Symp. Proc. Vol. 670, 2001 Materials Research Society, pp. K4.6.1 – K4.6.5. In addition, the instant inventor filed U.S. Patent Application No. 10/056,625, entitled *Multilayer High K Dielectric Films and Method of Making the Same*, on January 25, 2002, the entirety of which is hereby incorporated by reference, which describes high k stack dielectrics formed from hafnium oxide and hafnium silicon oxide. While an advance, zirconium oxynitride layers may react with underlying silicon either during deposition or during later manufacturing. Accordingly, further developments are needed.

### SUMMARY OF THE INVENTION

In general, the invention is directed to methods of fabricating gate and capacitor dielectrics for use in making advanced high-k structures in semiconductor devices. In one aspect, a metal alkylamide is used in a MOCVD or ALD process to create metal oxynitride and/or metal silicon oxynitride dielectric films. In another aspect, the present invention provides a device having a stack of high k materials.

In one embodiment, metal oxynitride layers are produced by reacting the metal alkylamide with an oxidant and a nitrogen source. Similarly, the metal silicon oxynitride layers are produced by reacting the metal alkylamide with a silicon tetraalkylamide, an oxidant and a nitrogen source.

The dielectrics may be employed to produce high-k stacked structures. In one embodiment, one or more metal oxynitride or metal silicon oxynitride layers are positioned intermediate between a silicon substrate and a doped polycrystalline silicon (Poly Si) layer. Alternatively, in another embodiment, the metal oxynitride or metal silicon oxynitride layers surround other metal oxide layers to form a complex dielectric intermediate that, in turn, lies between a silicon substrate and a Poly Si layer.

From the production point of view, MOCVD and ALD are more desirable processes than sputtering since sputtering requires a high vacuum system. Using MOCVD and ALD, metal oxynitride and metal silicon oxynitride can be deposited at relatively low temperatures (below  $500^\circ\text{C}$ ) and at approximately 1 Torr - which is much more practical for device production.

### BRIEF DESCRIPTION OF DRAWINGS

The invention will be described in detail in the following description and with reference to the following figures wherein:

**FIG. 1** is a schematic of a first high-k stack structure made in accordance with the present invention.

**FIG. 2** is a schematic of a second high-k stack structure made in accordance with the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

The invention is directed to gate and capacitor dielectrics for use in making advanced high-k stack structures using an MOCVD or ALD process. According to the invention, a metal alkylamide is used to create metal oxynitride or metal silicon oxynitride dielectric films. The metal in the metal alkylamide and the metal oxynitride or metal oxynitride films is selected from Hf, Ti, Zr, Y, La, V, Nb, Ta, W, Zn, Al, Sn, Ce, Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Preferably, the metal is selected from Hf, Ti and Zn. Even more preferably, the metal is either Hf or Zn.

In one embodiment, metal oxynitride layers are produced by reacting a metal alkylamide with an oxygen source and a nitrogen source. In another embodiment, metal silicon oxynitride layers are produced by reacting a metal alkylamide with a silicon source, an oxygen source and a nitrogen source.

From the production point of view, MOCVD and ALD are more desirable processes than sputtering which requires a high vacuum system. Using MOCVD and ALD, metal oxynitride and metal silicon oxynitride layers can be deposited at relatively low temperatures (below 500°C) and at approximately 1 Torr.

In general, the MOCVD method of the present invention comprises at least one cycle comprising the step of introducing the reactants into a deposition chamber containing the substrate upon which the films or layers are to be formed. The reactants include the metal alkylamide, the nitrogen source, the oxygen source and, if applicable, the silicon source. The reactants are introduced in the gas phase in one or more pulses. If the reactants are solid or liquid at room temperature, the necessary gases can be generated by direct vaporization in a vaporizer, with or without solvent, or by a bubbler. A film of desired thickness is deposited on the surface of the substrate material by repeating the deposition cycle as many times as necessary.

In one embodiment, the MOCVD method of the present invention comprises at least one cycle comprising the step of introducing the reactants into the deposition chamber at the same time. In another embodiment, the metal alkylamide is introduced to the deposition chamber in combination with at least one of the oxygen source and the nitrogen source and the remainder of the reactants are introduced into the deposition chamber in later steps.

The ALD process comprises at least one cycle comprising the following steps: (i) pulsing metal alkylamide gas into a deposition chamber comprising a substrate; (ii) purging the deposition chamber; (iii) introducing, in one or more additional pulses optionally separated by intermediate purges, an oxygen source, a nitrogen source and, optionally, a silicon source, to the deposition chamber; and (iv) purging the deposition chamber. Once again, the reactants are introduced in the gas phase in one or more pulses. If the reactants are solid or liquid at room temperature, the necessary gases can be generated by direct vaporization in a vaporizer, with or without solvent, or by a bubbler. ALD is carried out as follows: in the first step, a mono-layer of the metal alkyl amide is physi- or chemi-absorbed onto the surface of the substrate. In the second step any excess metal alkyl amide gas is removed by pulsing a non-reactive gas into the chamber and/or pumping gas out of the chamber using a vacuum pump. Suitable non-reactive gases include any noble gas and nitrogen gas. In the third step, the remaining reactants cleave undesired ligands from the precursor and add the oxygen, nitrogen and silicon necessary to form the desired oxynitride or oxynitride silicon layers. In the fourth step, excess reactants are removed from the chamber using a vacuum pump, an inert gas purge, or a combination of the two techniques. The result of each cycle is a mono-layer of the desired film. The cycle can be repeated as many times as necessary to achieve a film of desired thickness. In this manner film thickness and identity can be "nano-engineered" mono-layer by mono-layer.

The use of ALD has several advantages relative to MOCVD, namely, operability at comparatively low temperatures and the ability to produce conformal thin film layers on non-planar substrates. It is possible using ALD to control film thickness on an atomic scale and, thereby, "nano-engineer" complex thin films.

The process temperatures and pressures employed in the MOCVD and ALD processes can vary widely. In one embodiment the deposition temperature is from approximately 100°C to 500°C and preferably from approximately 200°C to 500°C.



Preferably, the deposition pressure is from approximately 100 mTorr to 10 Torr and more preferably from approximately 200 mTorr to 1.5 Torr.

Similarly, the vapor flow and pulse time for each pulse in each process can vary widely. In one embodiment the vapor flow is from approximately 1 sccm to 2000 sccm and preferably from approximately 5 sccm to 1000 sccm. Preferably, the pulse time is from approximately 0.01 s to 10 s and more preferably in the range of approximately 0.5 to 5 s.

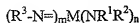
The substrates employed can be any material with a metallic or hydrophilic surface which is stable at the processing temperatures employed. Suitable materials will be readily evident to those of ordinary skill in the art. Preferred substrates include silicon wafers. The substrates may be pretreated to instill, remove or standardize the chemical makeup and/or properties of the substrate's surface. For example, silicon wafers form silicon dioxide on the exposed surfaces. Silicon dioxide in small amounts may be desirable because it attracts the metal precursor to the surface. However, in large quantities, silicon dioxide is undesirable. This is especially true when the layer formed is intended to be a substitute for silicon dioxide. Accordingly, silicon dioxide on the surface of silicon wafers is often stripped away, for example, by treatment with hydrogen fluoride (HF) gas prior to film formation. A thin standardized silicon dioxide surface layer, only a few Å thick, may then be reintroduced prior to film formation by standard oxidation methods, for example, by exposure to ozone.

A number of metal alkyamides can be used in the method of the present invention. Metal alkyamides are characterized by the presence of a metal group bonded through a single bond to at least one or more alkyl substituted nitrogen atoms.

Suitable metal alkyamides include compounds conforming to the following formulae or any mixture thereof:



and



where  $R^1$ ,  $R^2$  and  $R^3$ , independently, are selected from substituted or unsubstituted linear, branched, and cyclic alkyls and the like, where M is a metal selected from Hf, Ti, Zr, Y, La, V, Nb, Ta, W, Zn, Al, Sn, Ce, Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu, where p is an integer equal to a valence number for the metal, where m and n are integers and  $2m+n$  is equal to a valence number for the metal. Preferably, M is selected

from Hf, Zn and Ti, p is 4, m is 1 and n is 2. Even more preferably, M is either Hf or Zn. Preferably, R<sup>1</sup> and R<sup>2</sup> are, individually, a C<sub>1</sub>-C<sub>6</sub> alkyl.

The nitrogen source used in the method of the present invention can be any nitrogen source known in the art including but not limited to atomic nitrogen (N), ammonia (N<sub>3</sub>), hydrazine (H<sub>2</sub>NNH<sub>2</sub>), primary, secondary and tertiary alkyl amines, alkyl hydrazine and the like. Preferably, the nitrogen source is ammonia.

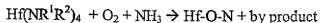
The oxygen source used in the method of the present invention can be any oxygen source known in the art including but not limited to atomic oxygen (O), oxygen gas (O<sub>2</sub>), ozone (O<sub>3</sub>), water (H<sub>2</sub>O), nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and the like. Preferably, the oxygen source is ozone.

The silicon source used in the processes of the invention can be any silicon source known in the art including silicon alkylamide, silane, disilane, dichlorosilane, SiCl<sub>4</sub>, SiHCl<sub>3</sub>, Si<sub>2</sub>Cl<sub>6</sub>, alkylsilane, aminosilane, Me<sub>3</sub>Si-N=N-SiMe<sub>3</sub> and the like. Preferably, the silicon source is silicon alkylamide. Suitable silicon alkylamides for use in the invention include those defined by the following formula:



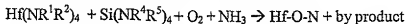
where R<sup>4</sup> and R<sup>5</sup> are selected, independently, from substituted and unsubstituted linear, branched, and cyclic alkyls. Preferably, R<sup>3</sup> and R<sup>4</sup> are selected, independently, from C<sub>1</sub>-C<sub>6</sub> alkyls.

By way of illustration, to form a hafnium oxynitride film, the following reaction can be performed using either the MOCVD or ALD process:



In other words, when hafnium alkylamide is exposed to an oxidant and a nitrogen source, a hafnium oxynitride film is formed. While Hf was used in this example, one skilled in the art will recognize that Hf may be substituted by any of the metals listed above.

Similarly, to form a hafnium silicon oxynitride film, the following reaction may be performed using either the MOCVD or ALD process:



In other words, when hafnium alkylamide is exposed to silicon alkylamide, an oxidant, and a nitrogen source, a hafnium silicon oxynitride film is formed. Once again, while Hf was used in this example, one skilled in the art will recognize that Hf may be substituted by any of the metals listed above.

A number of high-k stack structures can be made using the gate and capacitor dielectric materials made in accordance with the present invention. For example, metal oxynitride or metal silicon oxynitride layers may be sandwiched between a silicon wafer and layers of Poly Si. Alternatively, metal oxynitride or metal silicon oxynitride layers may surround metal oxide layers to form a dielectric intermediate which is, in turn, sandwiched between a silicon wafer and layers of Poly Si. These embodiments are visually illustrated in the attached figures.

**FIG. 1** is a schematic of a first high-k stack structure **100** made in accordance with the present invention. In **FIG. 1**, a silicon substrate **110** is coated with an intermediate layer **120** of hafnium oxynitride or hafnium silicon oxynitride. The intermediate layer, in turn is coated with an uppermost layer **130** of Poly Si. The intermediate layer **120** provides a high dielectric material between the highly conductive uppermost Poly Si layer **130** and the relatively less conductive silicon substrate **110**. While Hf is used in this example, it should be understood that Hf can be substituted by any of the metals listed above.

**FIG. 2** is a schematic of a second high-k stack structure **200** made in accordance with the present invention. In **FIG. 2**, a silicon substrate **210** is coated with a first intermediate layer **221** of hafnium oxynitride or hafnium silicon oxynitride. The first intermediate layer is coated with a second intermediate layer **222** of hafnium oxide. The second intermediate layer **222** is coated with a third intermediate layer **223** which, like the first intermediate layer **221** is composed of hafnium oxynitride or hafnium silicon oxynitride. Finally, the third intermediate layer **223** is coated with an uppermost layer **230** of Poly Si. The three intermediate layers, **221**, **222** and **223**, combine to form a high dielectric material between the highly conductive uppermost Poly Si layer **230** and the relatively less conductive silicon substrate **210**. While Hf was used in this example, it should be understood that Hf can be substituted by any of the metals listed above as well as others.

The preceding description is illustrative rather than limiting and is intended to provide a written description of the inventions sufficient to enable one of ordinary skill in the art to practice the full scope and any best mode of the inventions to which patent rights are claimed. Other embodiments and modifications may be readily apparent to those skilled in the art. All such embodiments and modifications should be considered

part of the inventions if they fall within the scope of the appended claims and any equivalents thereto.

Having thus described the invention with the details and particularity required by the patent laws, what is claimed and desired protected by Letters Patent is set forth in the appended claims.

**WHAT IS CLAIMED:**

1. A metal organic chemical vapor deposition process for forming a dielectric film on a substrate comprising at least one cycle comprising the step of introducing a metal alkyl amide, a nitrogen source, an oxygen source and, optionally, a silicon source, into a deposition chamber containing the substrate.

2. The process of claim 1 comprising at least one cycle comprising the step of introducing the metal alkyl amide, the nitrogen source, the oxygen source and, optionally, the silicon source, into the deposition chamber at the same time.

3. The process of claim 1 where the metal alkyamide is a metal alkylamide having one of the following formulae:



and



where  $R^1$ ,  $R^2$  and  $R^3$ , independently, are selected from substituted or unsubstituted linear, branched, and cyclic alkyls, where M is a metal selected from Hf, Ti, Zr, Y, La, V, Nb, Ta, W, Zn, Al, Sn, Ce, Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu, where p is an integer equal to a valence number for the metal, where m and n are integers and  $2m+n$  is equal to a valence number for the metal.

4. The process of claim 3 where the metal alkyl amide has the formula  $M(NR^1R^2)_p$ .

5. The process of claim 3 where the metal alkyl amide has the formula  $(R^3-N=)_mM(NR^1R^2)_n$

6. The process of claim 3 where M is selected from Hf, Zr and Ti, p is 4, m is 1 and n is 2.

7. The process of claim 3 where  $R^1$  and  $R^2$  are, individually, selected from  $C_1$ - $C_6$  alkyls.

8. The process of claim 3 where the nitrogen source is selected from ammonia, hydrazine and alkyl hydrazines, primary, secondary and tertiary alkyl amines, and atomic nitrogen.
9. The process of claim 3 where the oxygen source is selected from oxygen, oxygen gas, ozone, water, nitric oxide, nitrous oxide and hydrogen peroxide.
10. The process of claim 3 where the silicon source is selected from silicon alkylamide, silane, disilane, dichlorosilane,  $\text{SiCl}_4$ ,  $\text{SiHCl}_3$ ,  $\text{Si}_2\text{Cl}_6$ , alkylsilane, aminosilane and  $\text{Me}_3\text{Si-N=N-SiMe}_3$ .
11. The process of claim 10 where the silicon source is a silicon alkylamide defined by the following formula:

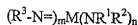


where  $\text{R}^4$  and  $\text{R}^5$  are selected, independently, from substituted and unsubstituted linear, branched, and cyclic alkyls.

12. An atomic layer deposition process for forming a dielectric film on a substrate comprising at least one cycle comprising the following steps:
- (i) pulsing metal alkylamide gas into a deposition chamber comprising a substrate;
  - (ii) purging the deposition chamber;
  - (iii) introducing, in one or more additional pulses optionally separated by intermediate purges, an oxygen source, a nitrogen source and, optionally, a silicon source, to the deposition chamber; and
  - (iv) purging the deposition chamber.
13. The process of claim 12 where the metal alkylamide is a metal alkylamide having one of the following formulae: of the following formulae:



and



where  $R^1$ ,  $R^2$  and  $R^3$ , independently, are selected from substituted or unsubstituted linear, branched, and cyclic alkyls, where M is a metal selected from Hf, Ti, Zr, Y, La, V, Nb, Ta, W, Zn, Al, Sn, Ce, Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu, where p is an integer equal to a valence number for the metal, where m and n are integers and  $2m+n$  is equal to a valence number for the metal.

14. The process of claim 13 where the metal alkyl amide has the formula  $M(NR^1R^2)_p$ .

15. The process of claim 13 where the metal alkyl amide has the formula  $(R^3-N)_mM(NR^1R^2)_n$ .

16. The process of claim 13 where M is selected from Hf, Zr and Ti, p is 4, m is 1 and n is 2.

17. The process of claim 13 where  $R^1$  and  $R^2$  are, individually, selected from  $C_1-C_6$  alkyls.

18. The process of claim 13 where the nitrogen source is selected from ammonia, hydrazine and alkyl hydrazines, primary, secondary and tertiary alkyl amines, and atomic nitrogen.

19. The process of claim 13 where the oxygen source is selected from oxygen, oxygen gas, ozone, water, nitric oxide, nitrous oxide and hydrogen peroxide.

20. The process of claim 13 where the silicon source is selected from silicon alkylamide, silane, disilane, dichlorosilane,  $SiCl_4$ ,  $SiHCl_3$ ,  $Si_2Cl_6$ , alkylsilane, aminosilane and  $Me_3Si-N=N-SiMe_3$ .

21. The process of claim 20 where the silicon source is a silicon alkylamide defined by the following formula:



where  $R^4$  and  $R^5$  are selected, independently, from substituted and unsubstituted linear, branched, and cyclic alkyls.

22. A metal oxynitride or metal silicon oxynitride film produced by the process in any one of claims 1 and 12.
23. A high-k stack structure comprising the following components:
- (i) a silicon wafer;
  - (ii) a metal oxynitride or metal silicon oxynitride film formed on the surface of the silicon wafer by the process in any one of claims 1 and 12; and
  - (iii) a Poly-Si layer formed on the metal oxynitride or metal silicon oxynitride layer.
24. A high-k stack structure comprising the following components:
- (i) a silicon wafer;
  - (ii) a first metal oxide layer formed on the surface of the silicon wafer;
  - (iii) a metal oxynitride or metal silicon oxynitride film formed on the surface of the first metal oxide layer by the process in any one of claims 1 and 12;
  - (iv) a second metal oxide layer formed on the surface of the metal oxynitride or metal silicon oxynitride layer; and
  - (v) a Poly-Si layer or a metal electrode layer formed on the second metal oxide layer.



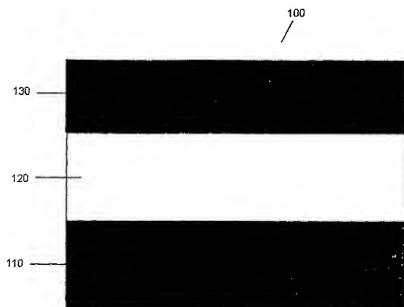


FIG. 1

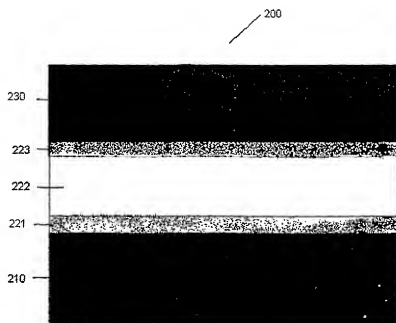


FIG. 2

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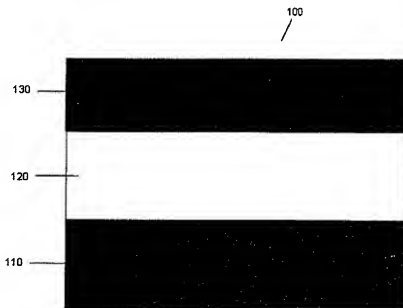
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#### Declaration under Rule 4.17:

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[Continued on next page]

(54) Title: METAL ORGANIC CHEMICAL VAPOR DEPOSITION AND ATOMIC LAYER DEPOSITION OF METAL OXYNI-  
TRIDE AND METAL SILICON OXYNITRIDE



(57) Abstract: The invention is directed to gate and capacitor dielectrics for use in making advanced high-k stack structures (100). According to the invention, a metal alkylamide is used in a MOCVD or ALD process to create metal oxynitride or metal silicon oxynitride dielectric film (120). The metal oxynitride or metal silicon oxynitride films can be positioned between a silicon substrate (110) and a doped polycrystalline silicon (Poly Si) or a metal electrode layer (130).

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US CL : 438/681,680,620,650,627 ; 427/255.31,255.394 ; 117/101, 104

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
---	US 6,616,972 B1 (SENZAKI et al ) 9 September 2003 (09.09.2003), the abstract, column 3 lines 8-20	----- 1-11.
Y		
---	US 6,624,072 B2 (VAARTSTRA) 23 September 2003 (23.09.2003), the abstract, fig 1, claims 1-6.	----- 1-11,22-24
Y		
---	US 6,534,395 B2 (WERKHOVEN et al ) 18 March 2003 (18.03.2003), the abstract, fig 1, fig 2, column 2 lines 23-29	----- 12-24
Y		
---	US 6,632,279 B1 (RITALA et al ) 14 October 2003 (14.10.2003) , the abstract, column 3 lines 40-44	----- 12-21
Y		

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☐ See patent family annex.

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